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MOLECULAR DIPOLE ELECTRETS

by

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## MOLECULAR DIPOLE ELECTRETS

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### ABSTRACT

The total polarization due to molecular dipoles in a glassy electret is computed using an Onsager cavity approach. From this result, all the possible contributions to the piezo- and pyroelectric coefficients are considered. It is shown that there are major contributions from the variation in dielectric constant and, for pyroelectricity, from thermal motion. These results account well for experimental data for polyvinyl chloride.



## INTRODUCTION

Solid organic materials which are cooled from the liquid state in the presence of an electric field form electrets. This behavior was first postulated by Heaviside<sup>1</sup> and confirmed by Eguchi.<sup>2</sup> These electrets have a permanent or slowly decaying electric polarization (dipole moment per unit volume) and, in general, exhibit piezoelectric and pyroelectric properties. That is, they respond electrically to mechanical and thermal stress, as was originally demonstrated experimentally for waxy solids<sup>3, 4</sup> and first explained with a simple dipole model.<sup>3</sup>

In recent years a variety of synthetic organic polymers have been shown to be piezoelectric and pyroelectric after suitable polarizing treatment.<sup>5, 6</sup> Even though the technology of making polymer film transducers has developed sufficiently to yield commercial instrumentation<sup>7</sup> and devices<sup>8</sup> there is still no consensus regarding the underlying mechanism on a molecular level nor is there a generally accepted equation relating transducer response to other basic structural or physical properties. Such an equation would aid in systematically adjusting parameters to optimize the effect and help predict limiting sensitivities.

Previous work on ceramic piezoelectric and pyroelectric materials like barium titanate and triglycine sulfate has provided a well established body of data and theory.<sup>9, 10</sup> Fukada has applied the classical group theory approach to polymers.<sup>11</sup> This formulation seems inappropriate for totally amorphous polymers, many of which form piezo- and pyroelectric electrets, and has not led to an understanding of fundamental behavior. A phenomenological model for polymers was published by Gubkin<sup>12</sup> and again the results did not adequately connect piezoelectricity to basic molecular properties. Aslaksen provided a theory for pyroelectricity in polyvinylidene fluoride (PVF<sub>2</sub>).<sup>13</sup> This theory described an important effect of molecular librations but did not include the volume effects originally described by Adams in his early



paper.<sup>3</sup> Other effects such as molecular reorientation<sup>14</sup> and charge injection<sup>15</sup> have also been proposed as contributing to piezo- and pyroelectricity in polymers.

In earlier papers<sup>6, 16</sup> we provided an equation connecting piezo- and pyroelectricity in amorphous polymers to dielectric, mechanical and thermal properties. The model was like that of Adams<sup>3</sup> and in addition included librational effects. The results for this model were deduced in an ad hoc manner however and missed an important contributing factor from the variation in dielectric constant. In this paper we treat the model rigorously and calculate the piezoelectric and pyroelectric responses from first principles.

Specifically the model is for an amorphous solid containing molecular dipoles which have been partially aligned in an electric field and then immobilized by cooling below the glass transition temperature. An expression for the permanent polarization is derived by means of a cavity reaction field calculation like that used by Onsager.<sup>17</sup> The temperature and pressure derivatives of this polarization yield the piezo- and pyroelectric coefficients in terms of other independently known physical properties. The pressure and temperature derivatives are shown to be closely related to each other as originally proposed.<sup>3</sup> The piezoelectric result is verified for an amorphous polymer. Verification of the pyroelectric result depends on knowing a value for a molecular libration amplitude, and a reasonable assumption about its value provides results that support the model.

#### PERMANENT POLARIZATION

Consider the model as illustrated in figure 1. A dipole with permanent moment  $\underline{\mu}$  and polarizability  $\alpha$  is at the center of a cavity of radius  $a$ . The cavity is embedded in a slab of medium with dielectric constant  $\epsilon$  and also has an electrical polarization  $\underline{P}$  in the  $z$  direction which is perpendicular to the plane of the slab. Any free charge that is trapped in the medium will be considered to be confined to the surface. Electrodes are applied to the surface and shorted together so that the applied field  $\underline{E}$  is equal to zero. There will be an internal field in the cavity  $\underline{F}$  acting on the dipole so that the total moment  $\underline{m}$  is given by



$$\underline{m} = \underline{\mu} + \alpha \underline{F} . \quad (1)$$

For this case, since there are no free charges in the interior of the dielectric, the potential can be written in the form

$$\phi = - \left( \frac{A}{r^2} + Br \right) \cos \theta , \quad (2)$$

where A and B are constants that will have different values in the external medium than in the cavity. Linearity and hence superposition will be assumed since fields commonly used to pole materials are still below those needed for saturation to be observed, and hysteresis effects are excluded. Then, the field in the cavity will be the superposition of the applied field, the permanent polarization and the dipole field. Following Frohlich,<sup>18</sup> we evaluate the potential assuming  $\underline{E}$ ,  $\underline{P}$  and  $\underline{\mu}$  are all present and parallel to each other. The boundary conditions are

$$\underline{E} = \underline{E}_0, \quad r \rightarrow \infty \quad (3)$$

$$\phi = \frac{m}{4\pi\epsilon_0} \frac{\cos \theta}{r^2}, \quad r \rightarrow 0, \quad (4)$$

$$\underline{D} = \epsilon_0 \underline{E} + \underline{P}, \quad r > a, \quad (5)$$

$$\underline{D} = \epsilon_0 \underline{E}, \quad r < a, \quad (6)$$

where  $\underline{D}$  is the electric displacement  $\epsilon_0$  is the permittivity of vacuum and  $\theta$  is the angle measured from the z axis to the dipole axis. Then, one can write

$$\phi = - \left( \frac{A}{r^2} + E_0 r \right) \cos \theta, \quad r > a, \quad (7)$$

$$\phi = - \left( \frac{m}{4\pi\epsilon_0 r^2} + Br \right) \cos \theta, \quad r < a. \quad (8)$$



One can evaluate  $A$  and  $B$  by imposing the conditions that the tangential component of  $\underline{E}$ ,  $E_\theta = -\frac{1}{r} \frac{\partial \Phi}{\partial \theta}$ , is continuous and the normal component of  $\underline{D}$ ,  $D_r = \epsilon_0 \epsilon \frac{\partial \Phi}{\partial r} + P_r$ , where  $P_r$  is the normal component of  $\underline{P}$ , must be continuous at  $a$ . For this last condition it should be remembered that  $\underline{P} = 0$  inside the cavity and  $\underline{P}$  is a constant outside the cavity. Then one finds that

$$\frac{A}{a^3} = \frac{(\epsilon - 1)}{(2\epsilon + 1)} E_0 + \frac{1}{(2\epsilon + 1)} \frac{P}{\epsilon_0} - \frac{3}{(2\epsilon + 1)} \cdot \frac{m}{4\pi \epsilon_0 a^3}, \quad (9)$$

$$B = \frac{3\epsilon}{(2\epsilon + 1)} E_0 + \frac{1}{(2\epsilon + 1)} \frac{P}{\epsilon_0} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \frac{m}{4\pi \epsilon_0 a^3}. \quad (10)$$

With this result, the Onsager derivation<sup>17</sup> can be suitably modified to allow for a permanent polarization. For the electret between shorted electrodes,  $\underline{E} = 0$  and the cavity field  $\underline{G}$  is now given by

$$\underline{G} = \frac{1}{(2\epsilon + 1)} \frac{P}{\epsilon_0}. \quad (11)$$

There is also a reaction field,  $\underline{R}$ , parallel to  $\underline{m}$  given by

$$\underline{R} = \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \frac{m}{4\pi \epsilon_0 a^3}. \quad (12)$$

This gives for the internal field  $\underline{F}$ ,

$$\underline{F} = \underline{G} + \underline{R} = \frac{1}{(2\epsilon + 1)} \frac{P}{\epsilon_0} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \frac{m}{4\pi \epsilon_0 a^3}. \quad (13)$$

Using Eq. 1, we obtain for the moment

$$\underline{m} = \mu_0 \underline{u} + \alpha \left[ \frac{1}{2\epsilon + 1} \frac{P}{\epsilon_0} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)a^3} \frac{m}{4\pi \epsilon_0} \right]. \quad (14)$$

where  $\underline{u}$  is a unit vector parallel to the permanent dipole and  $\mu_0$  is the magnitude of the permanent dipole moment. Solving for  $\underline{m}$  and using the relation

$$\alpha = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} 4\pi \epsilon_0 a^3, \quad (15)$$

we obtain for the total moment in the cavity



$$\underline{m} = \frac{(2\epsilon + 1)(\epsilon_{\infty} + 2)}{3(2\epsilon + \epsilon_{\infty})} \mu_o \underline{u} + \frac{4\pi a^3}{3} \frac{\epsilon_{\infty} - 1}{2\epsilon + \epsilon_{\infty}} \underline{P} \quad (16)$$

To obtain the total polarization it should be remembered that  $\underline{P}$  and  $\underline{m}$  are not parallel in general. However,  $\underline{P}$  is uniform throughout the dielectric and only the component of  $\underline{m}$  parallel to  $\underline{P}$  will not vanish on averaging. Then, since the material is composed of the dipoles,

$$\underline{P} = \frac{N}{V} \langle \underline{m} \rangle, \quad (17)$$

where  $N$  is Avogadro's Number and  $V$  is the molar volume. We allow the volume of the material to equal the sum of the volumes of the cavities so that

$$\frac{N}{V} \frac{4\pi a^3}{3} = 1. \quad (18)$$

If the average component of  $\underline{u}$  parallel to  $\underline{P}$  is given by  $\langle \cos \theta \rangle$ , then combining Eqs. 16, 17 and 18, we obtain

$$\underline{P} = \frac{(\epsilon_{\infty} + 2)(2\epsilon + 1)}{3(2\epsilon + \epsilon_{\infty})} \frac{N}{V} \mu_o \langle \cos \theta \rangle + \frac{\epsilon_{\infty} - 1}{(2\epsilon + \epsilon_{\infty})} \underline{P}, \quad (19)$$

where the vector notation has been suppressed since there is no question as to orientation. We can now solve for  $\underline{P}$  to give

$$\underline{P} = \frac{(\epsilon_{\infty} + 2)}{3} \frac{N}{V} \mu_o \langle \cos \theta \rangle \quad (20)$$

The result obtained for the permanent polarization using an Onsager type model is quite interesting. In the derivation, a distinction between  $\epsilon$  and  $\epsilon_{\infty}$  was kept although they are equal where no dipolar reorientation is allowed. This was done to show that all the terms involving the medium external to the cavity do



not enter the final expression. In fact the same result could have been derived from the Lorentz field  $\underline{F} = \underline{E} + \frac{1}{3} \frac{\underline{P}}{\epsilon_0}$  by letting  $E_\infty = 0$ . However, the case of frozen-in permanent dipolar polarization has not been recognized as leading to a Lorentz type field.

Also, it is interesting to compare the total polarization given in Eq. 20 with that of the Onsager liquid with free dipoles. The polarization of a fluid with permanent dipoles  $\epsilon$  can be written

$$P = \frac{N}{V} \langle m \rangle = \frac{(\epsilon_\infty + 2)(2\epsilon_L + 1)}{3(2\epsilon_L + \epsilon_\infty)} \frac{N}{V} \mu_o \langle \cos \theta \rangle + \frac{3\epsilon_L(\epsilon_\infty - 1)}{(2\epsilon_L + \epsilon_\infty)} \epsilon_o E \quad (21)$$

where  $\langle \cos \theta \rangle$  is carried explicitly and  $\epsilon_L$  is the liquid dielectric constant.

$$(\epsilon_L - 1) \epsilon_o E = P \quad (22)$$

Substituting Eq. 22 in Eq. 21 and solving for  $P$ , we obtain

$$P = \frac{(\epsilon_L - 1)}{(\epsilon_L - \epsilon_\infty)} \frac{(\epsilon_\infty + 2)}{3} \frac{N}{V} \mu_o \langle \cos \theta \rangle \quad (23)$$

When Eq. 23 is compared with Eq. 20, it is seen that at constant volume, the equations differ only by the factor  $\frac{(\epsilon_L - 1)}{(\epsilon_L - \epsilon_\infty)}$ . Therefore, if  $\langle \cos \theta \rangle$  is frozen in by going through a glass transition, at constant volume, one should freeze in a polarization equal to  $(\epsilon_L - \epsilon_\infty) \epsilon_o E_p$  where  $E_p$  is the poling field. This is exactly what one would predict from macroscopic arguments<sup>6</sup> and shows the consistency of the results for the electret with that of the Onsager fluid.

The last point that will be considered here is the question as to correlations between the dipoles of the electret. In a fluid this leads to the replacement in the Onsager formula of the factor  $\mu_o^2$  by  $g \mu_o^2$  where  $g$  is the average sum of projection cosines of all dipoles upon any reference dipole in the fluid. The  $g$  factor comes about from statistical mechanical averaging of squared total moment  $\langle \underline{PV} \cdot \underline{PV} \rangle$  at zero applied field to which the dielectric constant is related. In our notation,



this becomes  $N \langle \underline{m} \cdot \underline{\Sigma} \underline{m}_i \rangle$  where the index numbers all dipoles in the sample. It is the last factor in the angular brackets that leads to the  $g$  factor. By comparison with the development here where  $\langle \underline{PV} \rangle$  does not vanish for zero applied field the  $g$  factor must be contained in the  $\langle \cos \theta \rangle$  term of Eq. 20. In any event we expect the relation between Eq. 20 and Eq. 23 to still hold.

#### PIEZOELECTRIC AND PYROELECTRIC COEFFICIENTS

With the expression for the total polarization given by Eq. 20, it is possible to evaluate the change in surface charge with a uniform change in volume due to either a change in pressure or a change in temperature. That is, the change in surface charge with temperature or pressure is given by the change in  $\underline{P}$ .<sup>6</sup>

From Eq. 20,

$$\begin{aligned} \frac{\partial P}{\partial X} = & - \frac{N}{V^2} \frac{\epsilon_{\infty} + 2}{3} \mu_o \langle \cos \theta \rangle \frac{\partial V}{\partial X} \\ & + \frac{N}{3V} \mu_o \langle \cos \theta \rangle \frac{\partial \epsilon_{\infty}}{\partial X} \\ & + \frac{N}{V} \frac{\epsilon_{\infty} + 2}{3} \mu_o \frac{\partial \langle \cos \theta \rangle}{\partial X}, \end{aligned} \quad (24)$$

where  $X$  refers to either temperature or pressure. The permanent dipole moment  $\mu_o$  is assumed constant since the intra molecular force constants are much stronger than the inter molecular force constants. Also, unpublished dielectric measurements



on  $\text{CCl}_3\text{F}$  in this laboratory were carefully analyzed for possible variation of  $\mu_0$  with pressure and none could be found. Of the three terms in Eq. 24 only the last two need further evaluation and of these the second is the easiest to deal with. It has been shown<sup>19</sup> from pressure measurements on dipolar liquids over the range of densities considered here that,

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{C}{V} - \frac{D}{V^2} \quad (25)$$

C and D are constants for the material, and one can carry out the differentiation with respect to V to give

$$\frac{\partial \epsilon_\infty}{\partial X} = - \frac{1}{V} \left[ \frac{(\epsilon_\infty + 2)(\epsilon_\infty - 1)}{3} - \frac{D}{V^2} \frac{(\epsilon_\infty + 2)^2}{3} \right] \frac{\partial V}{\partial X} \quad (26)$$

The term involving D in (25) corrects the usual Clausius-Mossotti relation. Its value can be estimated for a particular polymer from data on structurally related simple liquids, and is relatively small.

Using (26) we can write (24) as,

$$\begin{aligned} \frac{\partial P}{\partial X} = & - \frac{N}{V^2} \mu_0 \langle \cos \theta \rangle \frac{\partial V}{\partial X} \left[ \frac{\epsilon_\infty + 2}{3} + \right. \\ & \left. \frac{(\epsilon_\infty + 2)(\epsilon_\infty - 1)}{9} - \frac{D}{V^2} \frac{(\epsilon_\infty + 2)^2}{3} \right] \\ & + \frac{N}{V} \frac{\epsilon_\infty + 2}{3} \mu_0 \frac{\partial \langle \cos \theta \rangle}{\partial X} \quad (27) \end{aligned}$$



Except for the small term containing  $D$ , the terms inside the bracket are of similar magnitude. The change in dielectric constant of the electret provides a major contribution to its piezo- and pyroelectric response.

#### EVALUATION OF $\langle \cos \theta \rangle$

The only term that remains to be evaluated in Eq. 24 is that involving  $\frac{\partial \langle \cos \theta \rangle}{\partial X}$ . In the discussion that follows any correlation contributions to  $\langle \cos \theta \rangle$ , such as the Kirkwood  $g$  factor will be ignored since they are liable to be small and require a more specific model than we are using.

The variability of  $\langle \cos \theta \rangle$  at constant dipole orientation may seem surprising, but fixed dipole orientation implies only that  $\langle \theta \rangle$  is constant. To evaluate  $\langle \cos \theta \rangle$  we will assume that the dipole is a classical rotational harmonic oscillator that oscillates about an angle  $\theta$  fixed with respect to the polarization direction. Consider the coordinate system shown in Fig. 2 where  $z$  is the direction of the permanent polarization and  $z'$  is the direction of the average position of the dipole. Then for a unit vector representing the dipole,  $\langle \cos \theta \rangle$  is equal to  $\langle z \rangle$ , the projection of the unit vector along the  $z$  axis. If the  $x'$  axis is chosen so that the dipole oscillates with amplitude  $\phi_0$  about the  $y'$  axis, then the dipole remains in the  $x'z'$  plane. Then from the definition of the Eulerian angles,

$$z = \sin \theta \sin \psi x' + \cos \theta z',$$

where  $z' = \cos \phi$  and  $x' = \sin \phi$ . If now  $\phi = \phi_0 \cos \omega t$ , then one obtains for the average projection

$$\begin{aligned} \langle z \rangle = \langle \cos \theta \rangle &= \frac{1}{\pi} \sin \theta \sin \psi \int_0^\pi \sin (\phi_0 \cos x) dx \\ &+ \frac{1}{\pi} \cos \theta \int_0^\pi (\phi_0 \cos x) dx. \end{aligned} \tag{28}$$



Eq. 28 is easily evaluated by noting that the first integral vanishes by symmetry and the second integral yields a Bessel Function of the first kind of zero order,  $J_0(\phi_0)$ . Therefore, one obtains

$$\langle \cos \theta \rangle = \cos \theta J_0(\phi_0). \quad (29)$$

Using the properties of Bessel Functions, the derivative is then evaluated as

$$\frac{\partial \langle \cos \theta \rangle}{\partial X} = - \cos \theta J_1(\phi_0) \frac{\partial \phi_0}{\partial X}, \quad (30)$$

where  $J_1(\phi_0)$  is the Bessel Function of the first kind and first order.

For a classical harmonic oscillator, the mean squared amplitude of vibration is given by

$$\langle \phi_0^2 \rangle = \frac{2kT}{I\omega^2} \quad (31)$$

where  $I$  is the moment of inertia. Replacing  $X$  with  $T$  we find

$$\begin{aligned} \left( \frac{\partial \phi_0}{\partial T} \right)_P &= \left( \frac{2kT}{I\omega^2} \right)^{-1/2} \left[ \frac{k}{I\omega^2} - \frac{2kT}{I\omega^3} \frac{\partial \omega}{\partial T} \right] \\ &= \frac{\phi_0}{2T} - \frac{\phi_0}{\omega} \left( \frac{\partial \omega}{\partial T} \right)_P \end{aligned} \quad (32)$$

Assuming the quasiharmonic approximation that the frequency depends only on volume by a Gruneisen constant  $\gamma = - (V/\omega) (d\omega/dV)$ , then Eq. 32 becomes

$$\left( \frac{\partial \phi_0}{\partial T} \right)_P = \frac{\phi_0}{2T} + \frac{\phi_0}{V} \gamma \left( \frac{\partial V}{\partial T} \right)_P \quad (33)$$



For  $X$  equal to  $p$ , the first term will not occur and we obtain

$$\left( \frac{\partial \phi_o}{\partial p} \right)_T = \frac{\phi_o}{V} \gamma \left( \frac{\partial V}{\partial p} \right)_T \quad (34)$$

The first term in Eq. 33 is large compared to the second, and hence the response to temperature will be greater than the response to pressure.

The final expression for the derivative of the polarization can now be written with the use of Eqs. 20, 27, 29 and 30 as

$$\begin{aligned} \frac{\partial P}{\partial X} = -P \left\{ \frac{1}{V} - \frac{\partial V}{\partial X} \left[ 1 + \frac{\epsilon_\infty - 1}{3} - (\epsilon_\infty + 2) \frac{D}{V^2} \right] \right. \\ \left. + \frac{J_1(\phi_o)}{J_o(\phi_o)} \frac{\partial \phi_o}{\partial X} \right\}, \quad (35) \end{aligned}$$

where  $\frac{\partial \phi_o}{\partial X}$  is given by either Eq. 33 or Eq. 34.

#### RELATION TO MEASURED QUANTITIES

While the derivation until now has been in terms of the polarization, the polarization is not a measured quantity. One customarily measures current, area and potential. If the polarization is uniform in the sample, then the total charge present on the surface due to the polarization is given by

$$Q = PA$$



where  $A$  is the area. Differentiating and using the relation

$$P = (\epsilon_L - \epsilon_\infty) \epsilon_o E_p = \Delta\epsilon \epsilon_o E_p$$

where  $E_p$  is the poling field used to form the electret, one obtains

$$\frac{1}{\epsilon_o E_p A} \frac{\partial Q}{\partial X} = \frac{\Delta\epsilon}{P} \frac{\partial P}{\partial X} + \frac{2}{3} \frac{\Delta\epsilon}{V} \frac{\partial V}{\partial X} \quad (36)$$

The assumption of isotropy has been used to convert the area derivative to a volume derivative.

This result can be combined with Eq. 35 to yield

$$\frac{1}{\epsilon_o E_p A} \frac{\partial Q}{\partial X} = - \frac{\Delta\epsilon}{V} \frac{\partial V}{\partial X} \left[ \frac{\epsilon_\infty}{3} - (\epsilon_\infty + 2) \frac{D}{V^2} \right] + \frac{\Delta\epsilon}{J_o(\phi_o)} \frac{J_1(\phi_o)}{J_o(\phi_o)} \frac{\partial \phi_o}{\partial X} \quad (37)$$

If  $\frac{1}{V} \frac{\partial V}{\partial X}$  is defined by  $V_X$ , Eq. 37 can be rewritten as

$$\frac{3}{\epsilon_o E_p A V_X} \frac{\partial Q}{\partial X} = - \Delta\epsilon \left[ \epsilon_\infty - 3(\epsilon_\infty + 2) \frac{D}{V^2} + \frac{3}{V_X} \frac{J_1(\phi_o)}{J_o(\phi_o)} \frac{\partial \phi_o}{\partial X} \right] \quad (38)$$



where  $V_X/3$  is the linear coefficient of expansion for the variable  $X$ . Equation 38 gives the desired result, the charge flow in an external circuit due to a change in either temperature or pressure in terms of the relevant material properties. Of these,  $\phi_0$  is the most difficult to measure. The term containing the constant  $D$  can be determined directly from dielectric and dilatometric measurements and, judging from materials where it has been measured, is probably small enough to be neglected. In a constant-temperature, variable-pressure experiment, the term in  $\phi_0$  is also small since  $\gamma$  for vibrations leading to  $\phi_0$  will be small. For pressure variation only the first term in the bracket will apply. For the constant-pressure, variable-temperature experiment there is an additional contribution from the term in  $\phi_0$ . For PVC<sup>16</sup> the results<sup>20</sup> are shown in Table I. It is seen that the theory adequately accounts for the piezoelectric data without adjustable parameters and that the angle  $\phi_0$  needed to account for the difference between the piezoelectric and pyroelectric results is quite reasonable. (Recent measurements on polyethylene gave  $\phi_0 = 10^\circ$ .<sup>21</sup>)

Thus, the model employed in this paper accounts in a reasonable manner for the electret properties due to frozen-in dipolar orientation in a glass of polar molecules.



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Table I

Results for PVC

$$\epsilon_L = 13, \quad \epsilon_\infty = 3$$

$\frac{3}{\epsilon_o E_p A V_X}$	$\frac{\partial Q}{\partial X}$	Measured	Predicted
X = p		27	30
X = T		44	44
( $\phi_o^2 >^{1/2} = 14^\circ$ )			



# ONSAGER CAVITY CALCULATION WITH FROZEN DIPOLES

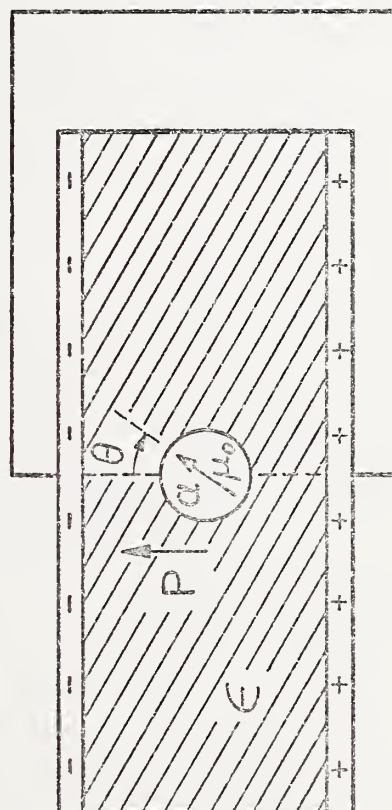


Fig. 1



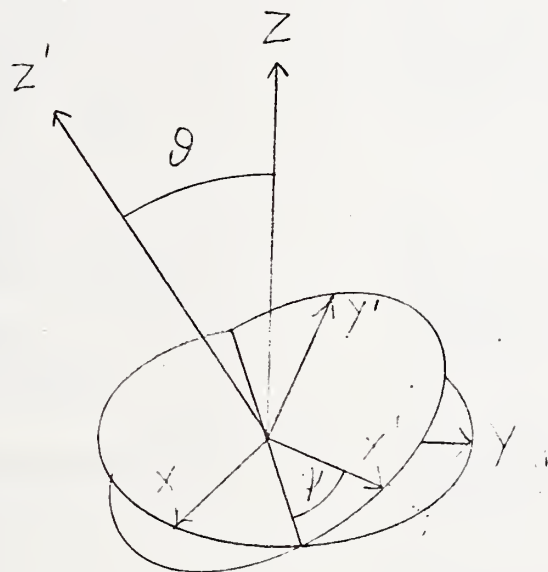


Fig. 2 Coordinates and Eulerian Angles for Librating Dipole



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